

PROCESS FOR PRODUCING IRON ORE AGGLOMERATES WITH USE OF SODIUM SILICATE
CONTAINING BINDER

The invention relates to a process for producing iron ore agglomerates.

5 Such a process is known from US 6,293,994, which discloses a process of making fired mineral pellets by mixing particulate mineral material with moisture and binder comprising substantially water-soluble organic polymer and alkali metal silicate in a dry weight amount which is either (a) above 0.13% based on moist mix or (b) above 0.08% based on moist mix and at least three times the dry weight of
10 substantially water-soluble organic polymer. The preferred polymer is a synthetic polymer formed of water-soluble ethylenically unsaturated monomer or monomer blend. The high amount of alkali metal silicate in the pellets described in US 6,293,994 generally is undesirable, because silicates can slow down the reduction process in steel making operations by blocking the pathways the reducing gases
15 use to permeate the pellet, which leads to an increase in energy costs. Furthermore, the use of such high amounts of alkali metal silicate results in green pellets that have a high tendency to deform, which in turn may lead to pellets of different size and shape, resulting in an inefficient process for preparing fired pellets.

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The object of the present invention is to provide iron ore agglomerates with improved physical properties.

The present invention provides a process for producing iron ore agglomerates
25 comprising agglomerating fine iron ore particles in the presence of a binder system wherein the binder system comprises a binder and an alkali metal silicate and wherein the alkali metal silicate is present in an amount of between 0.0001 to 0.08 percent by weight, based on the total weight of dry iron ore agglomerate, wherein the binder system is free of synthetic polymer. The process of the invention leads

to iron ore agglomerates with increased cold compression strength, preheat strength, and dry crush strength relative to the use of conventional binder systems comprising the same binder. Furthermore, small amounts of the alkali metal silicate are already sufficient to obtain a significant improvement in the physical properties of the agglomerates. Moreover, the specified amount of alkali metal silicate causes the agglomerates obtained with the process of the invention to have a similar or only slightly higher degree of deformation than binder systems where alkali metal silicate is absent. In contrast, binder systems comprising a larger amount of alkali metal silicate exhibit a significant increase in the degree of deformation, which is undesirable. In addition, the use of alkali metal silicate in accordance with the invention may enable a reduction of the amount of binder without a significant loss in physical properties of the obtained agglomerates.

The amount of alkali metal silicate preferably is at most 0.07 percent by weight (wt%), and most preferably at most 0.06 wt%, based on the total weight of dry iron ore agglomerate. By "dry iron ore agglomerate" is meant the total of all ingredients used in the formation of the iron ore agglomerate except water. Preferably, the amount of alkali metal silicate is at least 0.02 wt%, and most preferably at least 0.04 wt%, based on the total weight of dry iron ore agglomerate. It was found that pellets prepared using a binder system comprising at least 0.04 wt% of alkali metal silicate generally have a smooth surface and a higher resistance to abrasion, whereas pellets prepared using a binder system comprising less than 0.04 wt% of alkali metal silicate generally exhibit a rough surface, which can lead to the generation of fines or debris during processing of the formed pellets, e.g. during transport of the pellets.

The alkali metal silicate usually is a sodium silicate, but other alkali metal silicates can be used. Examples of sodium silicates are sodium metasilicate and the commercially available water glass. In the sodium silicates, the molar ratio

Na₂O:SiO₂ generally is in the range of 2:1 to 1:5, preferably in the range of 1:1 to 1:4. The amount of alkali metal silicate in the binder system generally is at least 1 wt%, preferably at least 10 wt%, and most preferably at least 15 wt%, and generally it is at most 99 wt%, preferably at most 85 wt%, and most preferably at most 75 wt%, based on the total weight of the binder system.

The alkali metal silicate preferably is well dispersed in the particles to be agglomerated. The silicate can be added to the iron ore particles in the form of a dry powder, an aqueous suspension, an aqueous solution, etc. Preferably, the alkali metal silicate is added in the form of an aqueous solution.

The binder in the binder system of the invention can be an inorganic binder or an organic binder, or a mixture thereof. Examples of inorganic binders are bentonite and hydrated lime. In the context of the present application alkali metal silicate is not considered to be an inorganic binder. Examples of organic binders are polymers including:

(1) Water-soluble natural polymers, such as guar gum, starch, alginates, pectins, xanthan gum, dairy wastes, wood related products, lignin, and the like;

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(2) Modified natural polymers such as guar derivatives (e.g. hydroxypropyl guar, carboxymethyl guar, carboxymethylhydroxypropyl guar), modified starch (e.g. anionic starch, cationic starch), starch derivatives (e.g. dextrin), and cellulose derivatives, such as alkali metal salts of carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethylhydroxyethyl cellulose, methyl cellulose, lignin derivatives (e.g. carboxymethyl lignin), and the like.

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The aforesaid polymers may be used alone or in various combinations of two or more polymers.

The binder system is free of synthetic polymers. Examples of synthetic polymers are polyacrylamides, such as partially hydrated polyacrylamides, methacrylamide and polymethacrylamide, polyacrylates and copolymers thereof, polyethylene
5 oxides, and the like.

A further aspect of the present invention is a process for producing iron ore agglomerates comprising agglomerating fine iron ore particles in the presence of a binder system wherein the binder system comprises carboxymethyl cellulose or a
10 salt thereof and an alkali metal silicate. The use of the combination of carboxymethyl cellulose and alkali metal silicate leads to agglomerates with increased physical properties, such as cold compression strength, preheat strength, and dry crush strength. In addition, the reducibility of the iron in the agglomerates generally is higher than is observed when a binder system
15 comprising an inorganic binder is used in the agglomeration process.

The invention further concerns a binder system comprising carboxymethyl cellulose and an alkali metal silicate. The amount of alkali metal silicate in the binder system generally is at least 1 wt%, preferably at least 10 wt%, and most
20 preferably at least 15 wt%, and generally it is at most 99 wt%, preferably at most 85 wt%, and most preferably at most 75 wt%, based on the total weight of the binder system.

The carboxymethyl cellulose or the salt thereof (both are referred to as "CMC") preferably is substantially water-soluble. Preferred salts of carboxymethyl cellulose
25 are alkali metal salts of carboxymethyl cellulose. Of these alkali metal salts the sodium salt is preferred. The CMC used in the present invention generally has a degree of substitution (the average number of carboxymethyl ether groups per repeating anhydroglucose chain unit of the cellulose molecule) of at least 0.4, preferably at least 0.5, and most preferably at least 0.6, and at most 1.5, more

preferably at least 1.2, and most preferably at most 0.9. Generally, the average degree of polymerization of the cellulose furnish is at least 50, preferably at least 250, and most preferably at least 400, and generally it is at most 8,000, preferably at most 7,000, and most preferably at most 6,000. It is more preferred to use
5 sodium carboxymethyl cellulose having a Brookfield viscosity in a 1% aqueous solution of more than 2,000 cps at 30 rpm, spindle #4. Still more preferred is sodium carboxymethyl cellulose having a Brookfield viscosity in a 1% aqueous solution of more than about 4,000 cps at 30 rpm, spindle #4.

10 A series of commercially available binders containing sodium carboxymethyl cellulose especially useful in the present invention is available from Akzo Nobel, under the trademark PeridurTM.

The manner in which the binder is added to the particulate material depends on the
15 type of material being agglomerated, the type of binder being used, and the desired results. For example, the binder may be added as a dry powder, an aqueous suspension, an aqueous solution, an aqueous gel, an aqueous sol (colloidal system), etc.

20 The amount of binder employed also varies with the results desired. For example, when an organic binder is used, the amount of binder may range from 0.0025 to 0.5 wt.%, based on the weight of the iron ore particles, with a preferred range being 0.005 to 0.2 wt.%. In the case of an inorganic binder, the amount of binder may range for example from 0.1 to 3 wt.%, based on the weight of the iron ore
25 particles.

The binder and the alkali metal silicate can be added to the iron ore particles together, one after the other, etc. This is not critical, so long as care is taken to

ensure that when the agglomeration takes place, the binder and the additive are present to perform.

The process of the invention is useful in agglomerating fine iron ore particles. The invention, however, is not limited to iron ores and is also useful in the agglomeration of fine particles of other metal ores. This invention is particularly well adapted for the agglomeration of materials containing iron, including iron ore deposits, ore tailings, cold and hot fines from a sinter process, iron oxides from dust collected in systems, or aqueous suspensions of iron ore concentrates from natural sources or recovered from various processes. Iron ore or any of a wide variety of the following minerals may form a part of the material to be agglomerated: taconite, magnetite, hematite, limonite, goethite, siderite, franklinite, pyrite, chalcopyrite, chromite, ilmenite, and the like.

The size of the material being agglomerated varies according to the desired results. For example, when the particulate material being agglomerated is iron ore, 100% of the particles may be less than 80 mesh, preferably, 90% are less than 200 mesh, and most preferably, 75% are less than 325 mesh.

It is also envisaged to use conventional additives, for instance a base such as sodium hydroxide, soda, or other additives such as sodium citrate, sodium oxalate, etc. These additives, their purpose, and their use are known to the skilled person.

Many processes for the agglomeration of particles, especially metal-based particles, are known in the art. Examples of such processes are pelletization, briquetting, sintering, etc. The binder system used in accordance with the invention is particularly suitable for pelletization. In the mining industry it is common practice to agglomerate or pelletize finely ground beneficiated mineral ore concentrate to facilitate processing and handling/shipping of the ore. After the mineral ore has

been mined, it is frequently wet ground to liberate and separate unwanted gangue minerals from the desired material, e.g. iron in the case of iron ore. The processed wet ground ore is screened to remove large particles, which can be recycled for further grinding. The screened fines are then vacuum filtered to reduce the moisture content to an acceptable range for pelletization. The filtered mineral ore is known in the art as "concentrate". A second process involves "dry grinding" and beneficiation of the mineral ore, in which case the moisture required for pelletization is added afterwards.

After beneficiation, a binding agent is added to the wetted mineral ore concentrate and the binder/mineral ore composite is conveyed to a balling drum or other means for pelletizing the ore. The binding agent serves to hold or bind the mineral ore together, so that the individual agglomerates can be transported without losing their integrity en route to further processing and induration.

Following the balling drum operation, the pellets are formed, but they are still wet. These wet pellets are commonly referred to as "green pellets" or "green balls". These green pellets are thereafter transported to a kiln and heated in stages to an end temperature of about 1,300-1,350°C. In the pelletizing process, the wet green pellets are loaded into the furnace for further processing. The moisture in the pellets is removed by induration at temperatures normally between 400-600°C. Following drying in the furnace, the pellets are transported to the preheat zone. This is an additional heating stage to further increase the pellets' hardness before they are transported to the kiln and/or final firing stage. Heating generally occurs at 900-1,200°C to bind the pellets together (e.g. to oxidize magnetite or crystallize hematite). From the preheat zone, the pellets are dropped 10-15 feet from the grate to the kiln. This is where the preheat strength is needed to prevent the pellets from chipping and breaking apart into dust particles. Finally, the preheated pellets are fired at a temperature of between 1,300 and 1,350°C.

The ability of the pellets to withstand breakage throughout processing can be approximated by performing standard tests that measure the strength the pellets will need at each stage of processing. (e.g. wet crush strength, dry crush strength, preheat strength, and cold compressive strength).

5 The present invention is illustrated in the following Examples.

Examples

10 In the following Examples green pellets of iron ore comprising various compounds in the amounts indicated in Table 1 were prepared. The green pellets were prepared by agglomerating iron ore concentrate in the presence of a binder and a binder additive. The amounts of binder and/or sodium silicate (in percent by weight) shown in Table 1 are based on the total weight of the iron ore concentrate. The iron ore concentrate employed in the Examples of Table 1 was Brazilian
15 hematite ore. The binder is Peridur 330 (ex Akzo Nobel), which comprises sodium carboxymethyl cellulose and sodium carbonate, and the sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2$ is 1:3.3) used in these experiments is supplied by PQ Corporation.

The process of making agglomerates are generally known to the skilled person.
20 The process is described in detail in US 6,071,325, which discloses a process of making agglomerates of 2,500 grams in a rotating airplane tire (approximately 40 cm diameter).

First the binder was mixed into the dry concentrate and homogenized. Then, the alkali metal silicate was mixed with the required amount of water (moisture content
25 between 8 and 9 wt%) and subsequently thoroughly mixed with the concentrate and the binder (using a Mullen Mixer model No. 1 Cincinnati Muller, manufactured by National Engineering Co. or the like). Pellet "seeds" were formed by placing a small portion of the concentrate in the rotating tire and adding atomized water to initiate pellet growth. Seed pellets with a size between 3.5 and 4 mm were retained
30 and kept apart for the formation of pellets with the desired size of 11.2 and 12.5

mm. Finished green pellets were produced by placing 165 grams of seed pellets described above in the rotating tire and adding a portion of the remaining concentrate mixture over a 3-minute growth period. Atomized water was added if necessary.

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Table 1

Comparative Example	Peridur TM (wt%)	Sodium silicate (wt%)
1	0.03	-
2	0.03	0.20
Example		
1	0.03	0.03
2	0.03	0.05
3	0.03	0.06
4	0.03	0.08

The moisture content, the drop number, and the wet and dry compressive strengths of the obtained green pellets were measured.

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Wet drop number

The Wet drop number was determined by repeatedly dropping a green pellet having a size between 11.2 and 12.5 mm from a height of 46 cm onto a horizontally placed steel plate until a visible crack formed in the pellet surface. The

15 number of times the pellet was dropped up to the point of fracture/cracking was determined. The average number of times averaged over 20 green pellets is referred to as the "Wet drop number".

Wet compressive strength

20 20 wet green pellets having a size of between 11.2 and 12.5 mm were stored in an airtight container. One by one the pellets were removed and placed in a standard measuring device in which a plunger of a scale was lowered onto the green pellet at a speed of 25 mm per minute. The maximum applied force at which the pellet

cracked was determined. The average force averaged over 20 green pellets is referred to as the Wet compressive strength.

Deformation

- 5 A minimum of 20 wet green pellets having a size of between 11.2 and 12.5 mm were stored in an airtight container. One by one the pellets were removed and placed in a standard measuring device in which a plunger of a scale was lowered onto the green pellet at a loading rate of 25 mm per minute. The machine (Model Lloyd Texture Analyser TA-Plus, controlled by PC with Nexygen version 4.5
10 software) is equipped with a 50 N load-cell and has a probe diameter of 10 mm. The deformation/deflection of the green pellet is recorded while increasing the force. The deformation is defined as the change in diameter of the green pellet at a force of 1 N, provided that the pellet is not ruptured at this point.

15 *Dry compressive strength*

- 20 20 green pellets having a size of between 11.2 and 12.5 mm were dried in an oven at 105°C for a minimum of two hours. Following drying, the dried pellets were placed one by one in a standard measuring device in which a plunger of a scale was lowered onto the green pellet at a speed of 25 mm per 10 seconds. The maximum applied force at which the pellet cracked was determined. The average force averaged over 20 green pellets is referred to as the Dry compressive strength.

The values obtained for the above parameters are tabulated in the Table below.

Table 2

Comparative Example	Moisture content (%)	Wet drop number	Deformation (mm)	Appearance green pellet	Dry compressive strength (kg/pellet)
1	8.6	2.7	0.22	rough, non-sticking	1.0
2	8.6	8.3	0.28	smooth, sticky	2.0
Example					
1	8.2	3.1	0.20	rough, non-sticking	1.2
2	8.3	4.1	0.24	smooth, non-sticking	1.9
3	8.3	5.6	0.23	smooth, non-sticking	2.9
4	8.1	4.9	0.24	smooth, non-sticking	3.3

- 5 From the above Table it can be deduced that the pellets of Examples 1-4, which are in accordance with the invention, show an increased dry compressive strength compared to the pellets obtained using a binder system comprising only the Peridur binder (Comparative Example 1). At the same time the pellets of Examples 1-4 show an improvement in wet drop number and only a slight increase in
- 10 deformation, whereas the pellets of Comparative Example 2 reveal a significantly higher deformation and wet drop number. Consequently, the pellets of Comparative Example 2 will be deformed in the steel making process to a much higher extent than the pellets of the invention, rendering the process for preparing fired pellets less efficient compared to processes using the pellets of the invention.
- 15 It is further noted that the appearance of the green pellets of Examples 2-4 is smooth and non-sticking, whereas the green pellets of Comparative Example 1 are rough. The pellets of Examples 2-4 will generate a lower amount of fines or debris, e.g. during transport of these pellets, compared to the pellets of Comparative

Example 1. Although the green pellets of Comparative Example 2 are smooth, they are sticky, causing undesirable clustering of the pellets during processing.